Characterization, Sources and Sinks of Colored Detrital Matter in the Ocean

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LONG-TERM GOALS

My primary research interest is the effect that phytoplankton community structure has on the optical fields and carbon cycling in the marine environment. Methods used in my lab are based on biomarkers, primarily chlorophylls, carotenoids and their degradation products. These are the chromophores which are responsible for a major fraction of the light absorbed in the ocean. It is my goal to characterize phytoplankton-derived chromophores in the marine environment and determine their effects on ocean optics and access their utility as biomarkers for the study of phytoplankton and processes associated with these in the ocean.

OBJECTIVES

The optical properties of the ocean are primarily determined by the optical properties of water, particles and dissolved matter. The absorption of light by particles is due to phytoplankton, colored detrital matter (CDetM) and minerals. Whereas the chromophores associated with phytoplankton have been studied extensively over the last 50 years, little is known about chromophores associated with CDetM even though these can contribute significantly to the absorption of light in the coastal zone. This project is a study of the nature and the sources and sinks of CDetM in the water column. The study's objectives are:

1. Characterize the chromophores of different classes of detrital matter, i.e., fresh and partially degraded fecal matter, resuspended sediments, particulate matter from below the euphotic zone and living organisms devoid of phytoplankton-derived pigments.

2. Search for specific chromophores that uniquely identify the different classes of detrital matter such that these marker-chromophores can be used to identify contributions of different classes of detrital matter to CDetM in the upper ocean.

3. Develop methods for the routine analysis and characterization of CDetM.

APPROACH

As potential sources of CDetM, phytoplankton, zooplankton, sediments and fecal material is subjected to chemical tests to identify and characterize the major chromophores associated with these. To characterize sinks, selected material is subjected to controlled microbial degradation and photooxidation.

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These experiments delineate the relevant time scales for these compounds in the water column as a function of temperature and light. Methods used to determine the relative contributions of phytoplankton, detrital chromophores and minerals to the absorption of light by particles in the ocean are tested using mixtures of phytoplankton and high- and low-carbon sediments.

WORK COMPLETED

Fecal matter from a variety of macrozooplankters, microzooplankters, sediment trap samples and sediments were analyzed, using recently developed methods, to map the distributions of chlorins in detrital matter. Likely degradation products of divinyl-chlorophyll *a* were chemically or biologically synthesized and characterized for the first time. To study the fate of divinyl-chlorophyll *a* in the marine environment its degradation products were traced from the euphotic zone through fecal matter, sedimenting detrital matter to surficial sediments.

RESULTS

The distribution of chlorins in different types of CDetM was surprisingly similar with the exception of carotenol-chlorin esters that were only found to be associated with the fecal matter of crustacean. This result implies that there are very few grazer-specific chlorins that could be used to trace the path of carbon through the marine food wed. In almost all types of detrital matter cyclic pheophorbides were the major contributor to total chlorins. This result is of importance for fluorescence based - laboratory or remotely sensed - methods for the detection of chromophores in the marine environment as cyclic pheophorbides do not fluoresce. Other major chlorin groups were pheophytin, pyropheophytin and pyropheophorbide. Allomers of these compounds were rarely detected. Pheophorbide is usually only present in small concentrations, suggesting that the loss of the C13^{2}-carbomethoxy group precedes the loss of the phytol.

The complement of chlorins in detrital matter derived from divinyl-chlorophyll *a* (Chl a_2 was usually very similar to the complement of chlorins derived from normal chlorophyll *a* (Chl a_1). This result is based on the analysis of microzooplankton fecal matter, sinking detrital matter and surficial sediments. This result suggests that the diagenesis of Chl a_2 is at least qualitatively very similar to the diagenesis of Chl a_1. Grazing experiments with microzooplankton suggest that the chlorin conversion efficiencies of the two molecules are also similar. This result and structural considerations suggest that the diagenesis of Chl a_2 is also quantitatively similar to the diagenesis of Chl a_1, i.e. reaction rates of the two molecules in the intestines of grazers or when associated with detrital matter are similar.

High relative concentrations of chlorins derived from Chl a_2 in detrital matter collected in sediment traps and in surficial sediment in the Eastern Tropical North Pacific, 18 to 26% of total chlorins, suggest that *Prochlorococcus*, the only wild-type photoautotroph with Chl a_2, contributes significantly to export production. Assuming that the diagenesis of Chl a_1 and Chl a_2 is qualitatively similar these results imply that the ratio of the direct contributions of *Prochlorococcus* and other autotrophs to export production is 0.25. The conclusion that the smallest photoautotroph, that contributes ~ 35% to autotroph biomass in this system, contributes significantly to export production is surprising as it should be assumed that carbon associated with picoautotrophs is primarily recycled within the microbial food web. Thus, it is quite likely that the microbial food web in the Eastern Tropical North Pacific is short-circuited by some macrozooplankter capable of grazing on picoautotrophs. Possible grazers are larvaceans.

IMPACT / APPLICATION

The work performed to date impacts currently used methods to measure Chl *a* degradation products in the ocean, methods used to partition the absorption of light by particles between phytoplankton and detrital contributions and it changes our view of chlorophyll diagenesis in the water column and sediments. The discovery of high concentrations of non-fluorescent cyclic pheophorbides in fecal matter suggests that the concept of 'pheopigments', as defined by analytical methods based on fluorescent detection, is inadequate. Complete quantification of Chl *a* degradation products requires chromatographic methods. Methods used to partition particulate absorption between phytoplankton and detritus overestimate the contribution of phytoplankton. These methods need to be improved. Current paradigms of chlorophyll diagenesis in recent and ancient sediments suggest that the structural diversity of porphyrins in ancient sediments is set by redox conditions in the sediment. However, structural considerations suggest that the structural diversity of sedimentary porphyrins may be set by rates of cyclic pheophorbide production relative to rates of pheophorbide / pheophytin production. Or restated, the structural diversity of porphyrins found in ancient sediments may rather be due to the action of grazers in the water column, rather than diagenesis in the sediments. The discovery of high concentrations of chlorins derived from Chl a_2 in sediments from the Eastern Tropical North Pacific might force us to reconsider the accepted paradigm of the marine food web.

RELATED PROJECTS

I have begun a detailed, NSF-funded study of carotenol-chlorin esters. The objectives are to prove the hypothesis that these are uniquely derived from the grazing of crustaceans on diatoms, to study the distribution of these in the marine environment and explore the stable isotope composition of these for paleoecological studies.

PUBLICATIONS

Goericke R., A. M. Shankle, D. J. Repeta, 1999. Novel carotenol chlorin esters in marine sediments and water column particulate matter. *Geochim. Cosmochim. Acta*, *63*: 2825 - 2834.

Goericke R., S. Strom, M. A.Bell, 2000. Distribution and sources of cyclic pheophorbides in the marine environment. *Limnol. & Oceanogr*. *45*: 200 - 211.

Goericke R., R. J. Olson, 2000. A. Shalapyonok, A novel niche for *Prochlorococcus* sp. in low-light suboxic environments in the Arabian Sea and the Eastern Tropical North Pacific, *Deep Sea Research* 47: 1183 - 1205.

Shankle A. M., R. Goericke, P. J. S. Franks, L. A. Levin. 2000. Chlorin distribution and degradation in sediments within and below the Arabian Sea oxygen minimum zone. subm. to *Deep-Sea Research*.

Goericke, R. 2000. Contributions of the cyanobacterium *Prochlorococcus* sp. to export production in the Eastern Tropical North Pacific. subm. to *Deep-Sea Research*.

Goericke, R. 2000. The early diagenesis of divinyl-chlorophyll *a* in the marine environment. subm. to *Marine Ecology Progress Series*.